PREPARATION, CHARACTERIZATION AND SOLUBILITY PRODUCT CONSTANT OF AMORCO3

ROBERT J. SILVA

This paper was prepared for submittal to AMERICIUM AND CURIUM CHEMISTRY

THE 1984 INTERNATIONAL CHEMICAL CONGRESS
OF PACIFIC BASIN SOCIETIES

December 12-16, 1984

January 12;. 1984

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

Unclassified

CIRCULATION COPY SUBJECT TO RECALL IN TWO WEEKS

DISCLAIMER

This document was prepared as an account of work spomored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or unefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government thereof, and shall not be used for advertising or product endorsement purposes.

PREPARATION, CHARACTERIZATION AND SOLUBILITY PRODUCT CONSTANT OF Amonco3

Robert J. Silva*
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550
USA

ABSTRACT. An investigation into the nature and solubility of a stable solid phase formed by a trivalent actinide, $^{243}\text{Am}^{3+}$, in dilute aqueous carbonate solutions was conducted. The compound exhibited an x-ray powder diffraction pattern which was nearly identical to that reported for NdOHCO3 - type A. The pattern could be indexed in the orthorhombic system with unit cell parameters a = 4.958, b = 8.487, and c = 7.215 Å. The steady state solubility of the compound was determined from the results of both dissolution and precipitation experiments. The average solubility product quotient for 0.1M ionic strength, $25 \pm 1^{\circ}\text{C}$ and I atmosphere pressure was found to be 583 ± 206 . The solubility product constant for zero ionic strength was estimated to be 335 ± 120 .

1. INTRODUCTION

Computer calculations indicate that the actinides U-Am will be the major contributors to the radioactivity of high-level nuclear waste after storage periods of several hundred years or longer [1, 2], the design criteria for the lifetime of the metal canisters [3]. In the event that the waste packages fail to contain the radioactive materials, they will enter the local groundwater system and, if moving, the groundwater is expected to provide the most likely mechanism by which the radionuclides could be transported from an underground storage facility to the accessible environment [4]. The actinides can react with various components in the altered groundwater to form insoluble phases that can control their solution concentrations and, thus, their migration rates. The exact nature of the solid phases will depend on a number of factors, e.g., the composition and redox properties of the groundwater system and the oxidation states of the actinides. Therefore, a knowledge of the nature and solubilities of actinide compounds that could form in groundwater is one of the pieces of information that is needed to predict migration rates.

Thermodynamic data on trivalent lanthanide elements [5], good analogs for actinides in the 3+ state [6], suggest that carbonate compounds of the latter may be quite insoluble in carbonate bearing groundwaters; however, no thermodynamic data have been reported. The object of this work was to investigate the nature and solubilities of compounds of a trivalent actinide, ²⁴³Am³⁺, in an aqueous carbonate system.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation and Characterization of Solid Phase

The preparation of rare-earth carbonates via the formation and subsequent hydrolysis of the trichloroacetate complex in aqueous solution is a well established method for producing a pure, easily filterable and crystalline material [7, 8]. The exact nature of the rare-earth carbonate depends on the atomic number of the rare earth and is quite sensitive to the preparative conditions, e.g., temperature, CO2 pressure and the washing procedure. The octahydrate, $R_2(CO_3)_3 \cdot 8H_2O_1$, is usually formed by the first members of the rare-earth series, e.g., La, while the dihydrate, $R_2(CO_3) \cdot 2H_2O$, is usually formed by the middle and end members of the series, e.g., Nd-Yb [9]. Charles has also reported that, even using the same procedures and conditions, some rare earths form the dihydrate, e.g., Nd, while others form the basic carbonate, ROHCO3, e.g., Pr [10]. The compounds are, however, usually pure. Because of these complications, it seemed prudent to first test the preparative method and the stability of the resulting solid phase with neodymium, a good analog element for americium.

Approximately 10 mgs of neodymium carbonate were prepared by the trichloroacetate method. An x-ray powder diffraction pattern of the material was obtained with a Debye-Scherrer camera using CuK_Q radiation ($\lambda=1.5418$ A) and a Ni filter. The d-spacings and relative intensities derived from the powder pattern are given in Table I under Nd Solid (I). Head and Holley have investigated the preparation and thermal decomposition of the rare-earth dihydrates [8, 9]. These elements were stated to form dihydrates that were isostructural and that had similar x-ray powder diffraction patterns. Unfortunately, these patterns were not published. However, an original x-ray film containing the powder diffraction pattern of the $Nd_2(CO_3)_3 \cdot 2H_2O$ (assigned from the results of chemical analysis) was recently obtained from C. E. Holley of LANL and analyzed. The d-spacings and relative intensities are given in Table I. Our material appeared to be pure, microcrystalline $Nd_2(CO_3)_3 \cdot 2H_2O$.

The Nd₂(CO₃)₃·2H₂O solid was placed in a polypropylene cell containing an aqueous solution composed of 0.1M NaClO₄ and 2xlO⁻⁴M HCO₃ at a pH of 6.12. After a contact time of three weeks, an x-ray powder diffraction pattern was again obtained on the solid. The resulting powder pattern is given in Table I under Nd Solid (II). The pattern was distinctly different from that of the Nd Solid (I) but nearly identical to the powder pattern reported for NdOHCO₃ - Type A [11].

TABLE I. X-RAY POWDER DIFFRACTION PATTERNS OF NA SOLID PHASES

	Nd2(CO3)3.5H2O		Nd Soli	d (1)	NdOHCO3ª Nd Solid (II)		(11)		
 	q(V)	Γp	q(V)	Ip	d(A)	Ic Ic	d(A)	I b	
	7.563	70	7,694	70	5.500	30	5.500	25	
	5.680	85	5.800	85	4,280	100	4.283	100	
	4.665	100	4.726	100	4.235	15	-	-	
	3.934	85	3.991	85	3.675	35	3.673	50	
	3.834	25	3.875	25	3,650	25	-	-	
	3.615	50	3.659	70	3,315	35	3,308	25	
	3.092	25	3.129	25	2.940	25	-	-	
	3.015	85	3.046	85	2.910	50	2.921	_. 50	
	2.976	10	-	-	2.748	3	-	-	
	2.873	10		-	2,630	30	2.634	25	
	2.751	25	2.767	25	2.475	25	2.482	25	
	2.582	70	2.607	50	2.400	10	2.404	10	
	2.249	10	-	-	2.323	40	2.324	50	
	2.170	10	-	-	2.310	18	-	-	
	2.082	10	-	-	2.138	7	-	-	
	2.016	50	2.031	35	2.122	9	-	-	
	1.982	25	1.994	25	2.097	1	•		
	1.872	35	1.882	35	2.050	40	2.050	35	
	1.825	35	1.835	35	2.030	13	-	-	
	1.779	35	1.789	35	1.984	40	1.988	35	
	1.737	25	1.745	35	1.925	25	1.929	10	
	1.562	35	1.566	25	1.880	10	1.885	10	
	-	_	••	_	1.830	19	1.828	25	

⁽a) Reference 11; (b) relative intensities visually estimated; (c) relative intensities by diffractometer.

There was no longer any evidence in the pattern for $Nd_2(CO_3)_3 \cdot 2H_2O$. The starting material had converted to the basic carbonate during the three week contact time.

An attempt was made to prepare $Am_2(CO_3)_3 \cdot 2H_2O$ by the same procedure as was used to prepare the $Nd_2(CO_3)_3 \cdot 2H_2O$. However, the x-ray powder diffraction pattern of the resulting Am compound was very similar to that of the $NdOHCO_3$ and not $Nd_2(CO_3)_3 \cdot 2H_2O$. The preparation of the solid was repeated with the Am, and the x-ray diffraction analysis of the solid gave a pattern again similar to the Nd basic carbonate. The d-spacings and relative intensities obtained from the pattern are given in Table II under Am Solid (I). Since the results with Nd suggested that the basic carbonate is more stable than the dihydrate in our aqueous carbonate system, no further attempts were made to produce the normal carbonate of Am.

2.2. Solubility Measurements

The solubility studies with trivalent americium were conducted in two parts. The first involved following to steady state the concentration of Am in a solution initially free of the element, i.e., undersaturation with respect to precipitation, but which had been placed in contact with the solid phase AmOHCO3. The second involved following to steady state the concentration of Am in a solution initially supersaturated in Am with respect to the precipitation of a solid phase but with no solid initially present. Much of the equipment and techniques used in these measurements have been described elsewhere [12].

In order to obtain a reliable value for the solubility product quotient for the reaction,

$$AmOHCO_3(s) + 2H^+ = Am^{3+} + H_2O + HCO_3^-$$

the pH range available for measuring the solubility was somewhat limited. It was necessary to hold the pH to less than about 6.5 to avoid significant hydrolysis of the ${\rm Am}^{3+}$ ion but greater than about 5 to avoid possible dissolution of all of the available starting solid (8 mgs). In addition, the ${\rm CO_3}^{2-}$ concentration was set sufficiently low so as to avoid significant carbonate complexation of the Am $^{3+}$ ion, i.e., $\sim 10^{-8} \text{M}$. A pH of 6.12 was selected as it is within a reasonably well buffered region where the concentrations of H2CO3 and HCO3 are equal. A computer controlled pH-stat was used to maintain a pH near this value. The bicarbonate, and thus carbonate, ion concentration was fixed by maintaining a gas mixture of 0.792 + .010% CO2 and 99.3% Ar over the aqueous phase. The equilibrium concentrations of bicarbonate and carbonate ions in the aqueous phase under these conditions were calculated to be $2.05 \times 10^{-4} \text{M}$ and $2.25 \times 10^{-8} \text{M}$, respectively, using reported carbonate equilibrium quotients for 0.1 M ionic strength [13, 14]. To fix the ionic strength, an aqueous solution of 0.1M NaClO4 was used as supporting electrolyte. Two titrations of 50 mls of the aqueous phase at a starting pH value of 6.14 with 0.100M HC1 to the end point of the HCO3 to H2CO3 conversion were made prior to the initiation of the solubility experiments. From the results, the

ĊΠ

TABLE II. X-RAY POWDER DIFFRACTION PATTERNS OF AMERICIUM SOLID PHASES

	Am Solid	Am Solid (I)		d (II)	I) Am Solid (III) Average (I, II, III) Calc		Calcula	ulated .	
	d(A)	I.a.	d(A)	I.	d(A)	Į a	d(V)	d(A)	hk1
	5.500	25	5.503	25	5.505	25	5.503 <u>+</u> 0.003	5.497	011
	4.283	100	4.279	100	4.281	100	4.281 <u>+</u> 0.002	4.281	110
	3.673	50	3.671	50	3.666	50	3.670 <u>+</u> 0.004	3.682	111
	-	-	-	-	-	-	-	3.658	021
	3.308	25	3.314	35	3.326	35	3.316 <u>+</u> 0.009	3.320	012
	-	-	2.942	25	-	-	-	2.943	121
	2.921	50	2.919	50	2.912	50	2.917 <u>+</u> 0.005	2.917	102
•	2.634	25	2.636	25	2.635	25	2.635 <u>+</u> 0.001	2.634	031
	2.482	25	2,480	25	2.475	25	2.479 <u>+</u> 0.004	2.479	200
	2.398	10	2,402	10	2.406	25	2.402 <u>+</u> 0.004	2.404	122
	2.324	50	2.335	35	2.331	50	2.330 <u>+</u> 0.006	2.326	131
	-	-	2.322	10	-	-	-	2.314	013
	•	-	2.134	10	2.132	25	2.133 <u>+</u> 0.002	2.141	220
	2,050	35	2.054	35	2.051	50	2.052 <u>+</u> 0.002	2.052	221
	1.988	35	1.986	25	. 1.985	25	1.986+0.002	1.986	212
	1.929	10	1.929	25	1.924	25	1.927+0.003	1.928	123
	1.885	10	1.889	10	-	-	1.887+0.003	1.883	141
	1.828	25	1.835	10	-	_	1.832+0.005	1.832	033

⁽⁼⁾ Relative intensities visually estimated.

bicarbonate ion concentration was calculated to be $2.67 \pm .16 \times 10^{-4} \underline{\text{M}}$. This value is in reasonable agreement with the concentration of $2.15 \pm .17 \times 10^{-4} \underline{\text{M}}$ calculated for the CO₂ partial pressure in the gas mixture at this pH.

2.3. Solubility Measurements from Unsaturation

Approximately 8 mgs of the crystalline AmOHCO3, Am Solid (I), were placed in a polypropylene cell with 50 mls of the aqueous phase at $25 \pm 1^{\circ}$ C and I atmosphere pressure. Two I ml aliquots of the aqueous phase were taken after 1, 3, 7, 14, 21, and 30 days equilibration time. After centrifugation at 15,000 RPM for 15 minutes, the Am concentrations were determined from the results of liquid scintillation counting of the supernates. The beta-emitting daughter, 239Np, was found not to be in nuclear decay equilibrium with the 243Am in solution at the times of sampling. Because the 239Np added to the measured total count rates of the aliquots, the samples required counting periodically for 3-4 weeks to allow secular equilibrium to be established so the appropriate counting corrections for the Np could be made.

At the end of the 30-day period, two additional 5 ml aliquots of the aqueous phase were taken. After centrifugation, the aliquots were split into two fractions. One fraction, 2 mls, was passed through a a 0.2 μ m acrodisc polysulfone filter while the other fraction, 3 mls, was passed through a 0.015 μ m Nuclepore polycarbonate filter. The first one-half of the fraction through the filters was discarded and a measured portion of the remaining filtrate analyzed for Am by liquid scintillation counting.

Also, at the end of the 30 day period, the solid phase remaining in the cell was subjected to x-ray diffraction analysis. The results obtained from the powder pattern are given in Table II under Am Solid (II). The powder pattern was identical to that of the starting material, Am Solid (I). There was no change in the solid phase during these dissolution measurements.

2.4. Solubility Measurements from Supersaturation

At the conclusion of the first part of the studies described above, the aqueous phase in the cell was made 0.1M in HClO4 to dissolve the solid AmOHCO3. The volume of the aqueous phase was adjusted to 50 mls by the addition of water and solutions of NaHCO3 and NaOH in such a manner as to again produce an aqueous phase 0.1M in NaClO4, 2xlO M in HCO3 and at a pH of 6.12. The remainder of the experiment proceeded as in the first part of these studies.

Aliquots of the aqueous phase were taken after 1, 3, 7, 14, 22, 31, 37, 44 and 51 days equilibration time in order to follow the Am solution concentration to steady state. At the 51 day period, in addition to separation of phases by centrifugation, aliquots were filtered as before. At this time, the solid phase that had precipitated was subjected to x-ray diffraction analysis. The information obtained from the powder pattern is given in Table II under Am Solid (III). The powder pattern was identical to that of Am Solid (I) and Am Solid (II).

RESULTS

3.1. Crystal Data

The corresponding d-values obtained from the x-ray powder diffraction patterns of the three solids, Am Solid I, II and III, were least square averaged; the results are given in Table II. Guided by the work on NdOHCO3 type A [11], the averaged values could be indexed in the orthorhombic system with the unit cell parameters a = 4.958, b = 8.487 and c = 7.215 Å. The calculated d-values and Miller indices are also given in Table II. The values of the parameters agree to within two decimal places with those given for NdOHCO3 - type A [11]. Thus, the Am solid was identified as AmOHCO3 and it is isostructural with NdOHCO3 - type A.

3.2. Solubility from Undersaturation

The results of the measurements of the solubility of the crystalline AmOHCO3 are given in Table III. The pH values given are the average values observed during each equilibration period. The errors in the pH values were estimated from the inherent reproducibility of measurements with the pH meter and electrodes, both on the dissolver solution and buffers, and from the root mean square deviations of pH values (measured every two hours) from the averages. No corrections were made for liquid junction potential differences.

The values and errors assigned to the Am solution concentrations are the average and deviations from the average of the two aliquots taken at each sampling period. The values of the bicarbonate concentrations were calculated from the partial pressure of CO_2 over the aqueous phase, i.e., $0.00792 \pm .0004$ atmospheres and the average pH value during the period.

Since the Am solution concentrations did not vary appreciably after the 7 day equilibration time, it was assumed that steady state had been achieved in the dissolution reaction. Some variation in the Am concentrations between equilibration times is due to differences in the pH. The Am concentrations of the solutions passed through the two different pore size filters at the 30 day period agreed to within experimental error. However, these values are only about 65% of the Am concentration of the centrifuged sample. Whether this difference was due to insufficient separation of solid and aqueous phases by our centrifugation system or due to loss of Am via absorption of soluble species by the filters was not determined. Since the source of this discrepancy was not known, the three values were given equal weight in subsequent data analysis.

3.3. Solubility from Supersaturation

The results of the measurements of the solution concentrations of Am as a function of equilibrium time during the precipitation of AmOHCO3 are given in Table IV. The values for the average pH, the Am concentrations and bicarbonate concentrations and their associated errors were obtained as described in the previous section.

TABLE III. RESULTS OF SOLUBILITY MEASUREMENTS BY DISSOLUTION OF Amonco3.

Equil. Time (days)	p#I	Conc. Am (moles/1)	Conc. IICO3 (moles/1)	Sol. Prod. Quot., Q _{BP}	log Q _{sp}
1	6.13 <u>+</u> .03	2.86 <u>+</u> .25x10 ⁻⁵	2.09 <u>+</u> .18×10 ⁻⁴	6.32 <u>+</u> .10x10 ³	3.80 <u>+</u> .06
3	6.13 <u>+</u> .03	1.19±.04x10 ⁻⁵	2.09 <u>+</u> .18x10 ⁻⁴	2.63 <u>+</u> .36x10 ³	3.42 <u>+</u> .06
7	6.15 <u>+</u> .03	2.17 <u>+</u> .54x10 ⁻⁶	2.19 <u>+</u> .19x10 ⁻⁴	5.51 <u>+</u> 1.56x0 ²	2.74+.11
14	6.13 <u>+</u> .03	2.39 <u>+</u> .21x10 ⁻⁶	2.09 <u>+</u> .18±10 ⁻⁴	5.28 <u>+</u> .85×10 ²	2.72 <u>+</u> .06
21	6.14 <u>+</u> .03	2.02 <u>+</u> .04x10 ⁻⁶	2.14 <u>+</u> .19x10 ⁻⁴	4.79 <u>+</u> .65x10 ²	2.68+.06
30	6.14 <u>+</u> .03	2.29±.03x10 ⁻⁶ (a)	2.14 <u>+</u> .19x10 ⁻⁴	5.43 <u>+</u> .73x10 ²	2.73 <u>+</u> .06
		1.54 <u>+</u> .13x10 ⁻⁶ (b)		3.65 <u>+</u> .58×10 ²	2.56 <u>+</u> .06
		1.40 <u>+</u> .13x10 ⁻⁶ (c)		3.32 <u>+</u> .55x10 ²	2,52 <u>+</u> .07

⁽a) Centrifugation; (b) centrifugation plus 0.2 µm filtration; (c) centrifugation plus 0.015µm filtration.

TABLE LV. RESULT OF SOLUBILITY MEASUREMENTS BY PRECIPITATION OF Amonico3.

Equil. Time (days)	рH	Conc. Am (moles/1)	Conc. HCO ₃ (moles/1)	Sol. Prod. Quot., Q _{SP}	log Q _{sp}
. 0	.009	6.61 <u>+</u> .21x10 ⁻⁴	-	-	
1	6.0 <u>9+</u> .03	3.66 <u>+</u> .13x10 ⁻⁴	1.91 <u>+</u> .17x10 ⁻⁴	6.14 <u>+</u> .82×10 ⁴	4.79 <u>+</u> .06
3	6.11 <u>+</u> .03	3.15 <u>+</u> .05x10 ⁻⁴	2.00+.18x10-4	6.07 <u>+</u> .82x10 ⁴	4.78 <u>+</u> .06
7	6.12 <u>+</u> .03	3.56±.13x10 ⁻⁴	2.05 <u>+</u> .18x10 ⁻⁴	7.35 <u>+</u> 1.02×10 ⁴	4.87 <u>+</u> .06
14	6.10 <u>+</u> .03	7.86+1.67x10-5	1.95±.17×10-4	1.41 <u>+</u> .35x10 ⁴	4.15 <u>+</u> .10
. 22	6.13 <u>+</u> .03	7.67 <u>+</u> .72×10 ⁻⁶	2.09±.18×10-4	1.70±.28x10 ³	3.23 <u>+</u> .07
31	6.14 <u>+</u> .03	3.21 <u>+</u> .14x10 ⁻⁶	2.14+.19x10-4	7.60 <u>+</u> 1.07x10 ²	2.88 <u>+</u> .06
37	6.13 <u>+</u> .03	4.42 <u>+</u> .17x10 ⁻⁶	2.09 <u>+</u> .18x10 ⁻⁴	9.77 <u>+</u> 1.36x10 ²	2.9 <u>9+</u> .06
. 44	6.13 <u>+</u> .03	4.71 <u>+</u> .30x10 ⁻⁶	2.09 <u>+</u> .18x10 ⁻⁴	1.04 <u>+</u> .15x10 ³	3.02 <u>+</u> .06 .
51	6.11 <u>+</u> .03	4.88 <u>+</u> .11x10 ⁻⁶ (a)	2.00 <u>+</u> .18x10 ⁻⁴	9.40 <u>+</u> 1.33x10 ²	2.97 <u>+</u> .06
		3.65±.06x10 ⁻⁶ (b)		7.03 <u>+</u> .95x10 ²	2.85 <u>+</u> .06
		3.20 <u>+</u> .32x10 ⁻⁶ (c)		6.16±1.03×10 ²	2.79 <u>+</u> .07

⁽a) Centrifugation; (b) centrifugation plus 0.2 µm filtration; (c) centrifugation plus 0.015 µm filtration.

As can be seen in Table IV, the Am concentrations decreased during the first month of the measurements but then remained relatively constant for the following 20 days. Therefore, it was assumed that steady state had been achieved.

As in the dissolution experiments, the Am concentrations measured for the filtered samples at the 51 day equilibration time agreed reasonably well but were only about 60% of the value measured for the centrifuged sample. The three values were given equal weight in subsequent data analysis.

3.4. Evaluation of the Solubility Product Quotient and Constant

Solubility product quotients, Q_{SD} , were calculated from the measured concentrations given in Table III and IV for the following reaction

$$AmOHCO_3(s) + 2H^+ = Am^{3+} + HCO_3^- + H_2O$$
 (1)

The concentrations of hydrogen ion were derived from the measured pH values using an activity coefficient of 0.78. This value was estimated from trends in mean activity coefficients for 0.1M HCl [15], 0.1M HClO₄ [15] and HCl in 0.1M NaCl [16].

Since the Am³⁺ ion can undergo a small amount of hydrolysis and carbonate complexation under the solution conditions of the experiment, estimates of the degree of these reactions were made. The first hydrolysis constant for Am³⁺ has not been measured in a noncomplexing medium at 0.1M ionic strength; however, a log value of -7.7 + 0.3 has been reported for Cm³⁺ [17]. Since Am³⁺ and Cm³⁺ are adjacent actinides of similar ionic radii, that of Am being slightly larger, a value of -7.8 + 0.3 was assumed for Am³⁺. From this quotient, the AmOH²⁺ to Am³⁺ concentration ratio for a pH of 6.12 was calculated to be 0.016 + 0.012.

A log value of 5.81 \pm 0.04 has been reported for the formation constant, 1, of the first carbonate complex of Am in 1M NaClO4 [18]. Unfortunately there are no data on mean activity coefficients of appropriate Am salts in mixed electrolyte systems which could be used to correct the quotients obtained in 1M NaClO4 to 0.1M NaClO4. As the next best approximation, it was decided to use mean activity coefficients of LaCl3-HCl mixtures that have been measured experimentally [19]. The mean activity coefficient for appropriate carbonate species in a mixed electrolyte were estimated using Pitzer's equations [20]. Ion interaction parameters used in the calculations for carbonate species [21] and NaClO4 [22] are reported in the literature. The single ion activity coefficient for AmCO3 was taken to be equal to that of Na The resulting estimate for log β_1 (0.1M) was 6.11 \pm 0.04. This quotient leads to a value of 0.027 \pm 0.003 for the AmCO3 to Am 3+ concentration ratio.

From the above ratios, the concentration of free Am $^{3+}$ was calculated as 95.9 \pm 1.3% of the measured Am in solution. The total Am solution concentrations given in Tables III and IV were reduced by this percentage before calculation of the $Q_{\rm SD}$'s given in the tables.

The $Q_{\rm Sp}$ values calculated from the data obtained by the three different solid-solution separation schemes at the 30-day equilibration time for the dissolution experiment and the 51-day equilibration time for the precipitation experiment were averaged by the least squares method. The resulting mean and standard deviation of the solubility product quotient for 0.1 M ionic strength was 583 ± 206 . Estimates for the activity coefficients of Am^{3+} , HCO_3 and H^+ at 0.1 M ionic strength were used to obtain an approximate value for the solubility product constant, $K_{\rm Sp}$, at zero ionic strength from the solubility product quotient given in the preceeding paragraph. The sources of the estimated activity coefficients were given previously in this paper. Values of 0.46, 0.76, and 0.78 were used for Am^{3+} , HCO_3^- and H^+ , respectively. The resultant value for $K_{\rm Sp}$ was 335 ± 120 .

4. CONCLUSIONS

The basic carbonate of americium, AmOHCO3, was found to be a stable solid phase in dilute aqueous carbonate solutions at near neutral pH. The compound is isostructural with NdOHCO3 - type A and its x-ray diffraction pattern can be indexed in the orthorhombic system. The solubility product quotient for 0.1M ionic strength, $25 \pm 1^{\circ}C$ and 1 atmosphere pressure was found to be 583 ± 206 . The solubility product constant for zero ionic strength was estimated to be 335 ± 120 .

5. ACKNOWLEDGEMENTS

The author wishes to thank C. E. Holley, Jr., of the Los Alamos National Laboratory for making available the x-ray film of the powder diffraction pattern of Nd₂(CO₃)₃·2H₂O. The help of A. Zalkin of the Lawrence Berkeley Laboratory in the interpretation of powder patterns is gratefully acknowledged. Thanks are due J. J. Bucher (LBL) for helpful advise on estimating activity coefficients and H. Nitsche (LBL) for calculations involving Pitzer's equations. This work was supported by the office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, while the author was employed by the Lawrence Berkeley Laboratory.

*Work supported by the Division of Health, Siting and Waste Management, Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission under contract FIN No. B 3040-0 at Lawrence Berkeley Laboratory and by the Department of Energy under Contract W-7405-Eng-48 at the Lawrence Livermore National Laboratory.

6. REFERENCES

- 1. Little, A. D., 1977. Technical Support of Standards for High-Level Waste Management, Vol. A, Source Term Characterization. EPA Report 520/4-79-007A. United States Environmental Protection Agency, Office of Nuclear Waste Isolation, Washington D.C., 20460
- 2. NRC, 1983. Staff Analysis of Public Comments on Proposed Rule

 10CFR Part 60, Disposal of High-Level Radioactive Wastes in

 Geologic Repositories. U.S. Nuclear Regulatory Commission

 Report, NUREG-0804, Washington, D.C., p. 467.
- 3. U.S. Nuclear Regulatory Commission, 1983. 10CFR Part 60, Disposal of High-Level Radioactive Wastes in Geologic Repositories, Technical Criteria. Section 60.113, Performance of Particular Barriers after Permanent Closure, Federal Register, Vol. 48 (No. 120), p. 28224.
- 4. Klingsberg, C., and J. Duguid, 1980. Status of Technology for Isolating High-Level Radioactive Wastes in Geologic Repositories, DOE/TIC-11207, U.S. Department of Energy, Washington D.C., p. 15.
- 5. Smith, R. M., and A. E. Martell, 1976. <u>Critical Stability Constants</u>, Vol. 4, <u>Inorganic Complexes</u>, Plenum Press, New York, p. 37.
- 6. Kutz, J. J. and G. T. Seaborg, 1957. The Chemistry of the Actinide Elements, Wiley and Sons, New York, p. 406-475.
- 7. Salutsky, M. L., and L. L. Quill, 1950. 'The Rare-Earth Metals and their Compounds. XII. Carbonates of Lanthanum, Neodymium and Samarium', J. Amer. Chem. Soc., 72, p. 3306-3307.
- 8. Head, E. L., and C. E. Holley, Jr., 1963. 'The Preparation and Thermal Decomposition of Some Rare-Earth Carbonates'. Rare-Earth Research III, Gordon and Breach, N.Y. pp. 51-63.
- 9. Head, E. L., and C. E. Holley, Jr., 1964. 'The Preparation and Thermal Decomposition of the Carbonate of Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc.', Rare-Earth Research IV, Gordon and Breach, N.Y., pp. 707-718.
- 10. Charles, R. G., 1965. 'Rare-Earth Carbonates Prepared by Homogeneous Precipitation', J. Inorg. Nuclear Chemistry, 27, pp. 1489-1493.
- 11. Dexpert, H. and P. Caro, 1974. 'Determination de la Structure Crystalline de la Variete a des Hydroxycarbonates de Terres Rares LnOHCO3', Mat. Res. Bull., 9, pp. 1577-1586.

- 12. Silva, R. J., and A. W. Yee, 1982. Geochemical Assessment of

 Nuclear Waste Isolation, 'Testing of Methods for the
 Separation of Solid and Aqueous Phases a Topical
 Report', NUREG/LBL-14696, Lawrence Berkeley Laboratory,
 Berkeley, CA.
- 13. Harned, H. S. and R. Davis, Jr., 1943, 'The Ionization Constant of Carbonic Acid in Water and the Solubility of Carbon Dioxide in Water and Aqueous Salt Solutions from 0 to 50°'. J. Am. Chem. Soc., 65, pp. 2030-2037.
- 14. Phillips, S. L., 1982. Hydrolysis and Formation Constants at 25°C.

 Lawrence Berkeley Laboratory report LBL-14313, Berkeley, CA,
 p. 50.
- 15. Robinson, R. A. and R. H. Stokes, 1959. <u>Electrolyte Solutions</u>, Appendix 8.10, Butterworth, London, pp. 491-492.
- 16. Harned, H. S. and B. B. Owen, 1958. The Physical Chemistry of Electrolyte Solutions. Table 14-2-1A, Reinhold, N.Y., p. 748.
- 17. Edelstein, N. J. Bucher, R. Silva, and H. Nitsche, 1982.

 Thermodynamic Properties of Chemical Species in Nuclear Waste:

 Topical Report. ONWI/LBL-14325, Office of Nuclear Waste

 Isolation, Battelle Memorial Institute, Columbus, Ohio, p. 50.
- 18. Lundquist, R., 1982. 'Hydrophilic Complexes of the Actinides. I. Carbonates of Trivalent Americium and Europium', Acta Chem. Scand., A36, p. 741-750.
- 19. Khoo, K. H., T. K. Lim and C. Y. Chan, 1981. 'Activity Coefficients in Aqueous Mixtures of Hydrochloric Acid and Lanthanum Chloride at 25°C'. J. Sol. Chem., 10, pp. 683-691.
- 20. Pitzer, K. S., 1973. 'Thermodynamics of Electrolytes. I.
 Theoretical Basis and General Equations'. J. Phys. Chem., 77
 (No. 2), pp. 268-277.
- 21. Pitzer, K. S., and G. Mayorga. 1973. 'Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes With One or Both Ions Univalent', J. Phys. Chem., 77 (No. 19), pp. 2300-2308.
- 22. Peiper, J. L. and K. S. Pitzer, 1982. 'Thermodynamics of Aqueous Carbonate Solutions Including Mixtures of Sodium Carbonate, Bicarbonate and Chloride', J. Chem. Thermodynamics, 14, pp. 613-638.